

Adhesives for refrigerated substrates

The invention relates to the use of free-radically polymerized,  
5 UV-crosslinkable addition polymers which consist to the extent of  
at least 50% by weight of C<sub>2</sub> to C<sub>18</sub> alkyl (meth)acrylates as  
adhesives for the bonding of carriers coated with the polymer on  
substrates, wherein from 0.1 to 30% by weight of the monomers of  
which said polymer is composed are monomers A without carboxylic  
10 acid or carboxylic anhydride groups and with a water solubility  
of more than 5 g of monomers per liter of water and said  
substrates are moist substrates, especially refrigerated  
substrates.

15 UV-crosslinkable polymers and their use as adhesives - as  
hot-melt pressure-sensitive adhesives, for example - are known  
from DE-A-2 411 169, EP-A-246 848, DE-A-4 037 079 or DE-A-3 844  
444, for example.  
20 These adhesives have not been used to date for moist substrates,  
especially refrigerated substrates.

For producing labels for refrigerated product it is normal to use  
block polymers of the styrene-isoprene-styrene or  
25 styrene-butadiene-styrene type. A general disadvantage of these  
block copolymers lies in their softness, which leads to  
difficulties in the course of processing and use.

There is a desire for alternative polymers as adhesives for  
30 moist, refrigerated substrates.

It is an object of the present invention to provide alternative  
polymers for such a use.

35 We have found that this object is achieved by the use defined at  
the outset.

For crosslinking with UV light, the addition polymer may contain  
a photoinitiator. The photoinitiator may be attached to the  
40 polymer but may also be unattached and merely mixed with the  
polymer.

Customary photoinitiators that can be added to the polymer are,  
for example, acetophenone, benzoin ethers, benzil dialkyl ketals,  
45 or derivatives thereof.

The amount of photoinitiator mixed in is preferably from 0.05 to 10 parts by weight, with particular preference from 0.1 to 2 parts by weight, per 100 parts by weight of polymer.

5 Through irradiation with high-energy light, especially UV light, the photoinitiator or photoinitiator group brings about a crosslinking of the polymer, preferably by means of a chemical grafting reaction of the photoinitiator group with a spatially adjacent polymer chain. Crosslinking can be effected in  
10 particular by inserting a carbonyl group of the photoinitiator into an adjacent C-H bond to form a -C-C-O-H grouping.

The wavelength range within which the photoinitiator group can be activated, i.e., that in which the principal absorption band of  
15 the photoinitiator group lies, is preferably from 200 to 450 nm, with particular preference from 250 to 350 nm, with very particular preference from 250 to 280 nm.

Preferably, the photoinitiator is attached to the polymer.  
20 The polymer is obtainable by free-radical addition polymerization from ethylenically unsaturated free-radically polymerizable compounds.  
25 In the preferred case where the photoinitiator is attached to the polymer an ethylenically unsaturated compound having a photoinitiator group is preferably incorporated by copolymerization.

30 The UV-crosslinkable polymer consists preferably to the extent of from 50 to 99.85% by weight, preferably from 60 to 99.4% by weight, with very particular preference from 80 to 98.9% by weight, of C<sub>2</sub> to C<sub>18</sub> alkyl (meth)acrylates. Preference is given to C<sub>2</sub>-C<sub>10</sub> alkyl (meth)acrylates, e.g., n-butyl acrylate, ethyl  
35 acrylate, and 2-ethylhexyl acrylate. Mixtures of the alkyl (meth)acrylates are used in particular.

In the case of the copolymerized photoinitiator the addition polymer further consists to the extent of from 0.05 to 10% by  
40 weight, preferably from 0.1 to 2% by weight and with particular preference, from 0.1 to 1% by weight, of ethylenically unsaturated compounds having a photoinitiator group.

The ethylenically unsaturated compound having a photoinitiator  
45 group is preferably an acetophenone derivative or, with particular preference, a benzophenone derivative.

Suitable compounds are acetophenone or benzophenone derivatives containing at least one - preferably one - ethylenically unsaturated group. The ethylenically unsaturated group is preferably an acrylic or methacrylic group.

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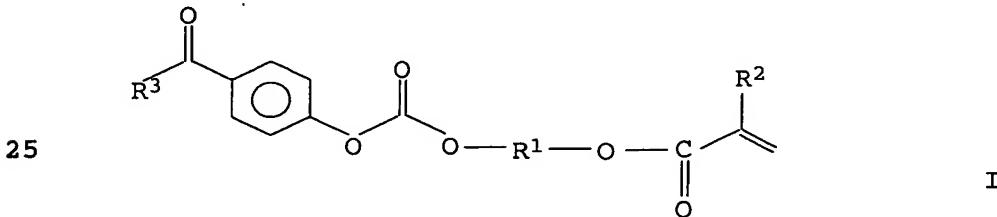
The ethylenically unsaturated group can be attached directly to the phenyl ring of the acetophenone or benzophenone derivative. In general, there is a spacer group situated between phenyl ring and ethylenically unsaturated group.

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The spacer group can contain, for example, up to 100 carbon atoms.

Suitable acetophenone or benzophenone derivatives are described, 15 for example, in EP-A-346 734, EP-A-377199 (1<sup>st</sup> claim), DE-A-4 037 079 (1<sup>st</sup> claim) and DE-A-3 844 444 (1<sup>st</sup> claim) and are incorporated by this reference into the present specification. Preferred acetophenone and benzophenone derivatives are those of the formula

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where R<sup>1</sup> is an organic radical having up to 30 carbon atoms, R<sup>2</sup> is 30 a hydrogen atom or a methyl group, and R<sup>3</sup> is an unsubstituted or substituted phenyl group or a C<sub>1</sub>-C<sub>4</sub> alkyl group.

With particular preference, R<sup>1</sup> is an alkylene group, especially a C<sub>2</sub>-C<sub>8</sub> alkylene group.

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With particular preference, R<sup>3</sup> is a methyl group or a phenyl group.

The addition polymer may further include ethylenically 40 unsaturated compounds as structural components. Mention may be made, for example, of vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinyl aromatics having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, vinyl ethers of alcohols containing 1 to 10 carbon atoms, aliphatic 45 hydrocarbons having 2 to 8 carbon atoms and 1 or 2 double bonds, or mixtures of these monomers.

Examples of vinyl esters of carboxylic acids having 1 to 20 carbon atoms are vinyl laurate, vinyl stearate, vinyl propionate, Versatic acid vinyl esters, and vinyl acetate.

5 Suitable vinylaromatic compounds are vinyltoluene,  $\alpha$ - and  $p$ -methylstyrene,  $\alpha$ -butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene and, preferably, styrene. Examples of nitriles are acrylonitrile and methacrylonitrile.

10 The vinyl halides are chloro-, fluoro- or bromo-substituted ethylenically unsaturated compounds, preferably vinyl chloride and vinylidene chloride.

15 Examples of vinyl ethers are vinyl methyl ether and vinyl isobutyl ether. Preference is given to vinyl ethers of alcohols containing 1 to 4 carbon atoms.

As hydrocarbons having 2 to 8 carbon atoms and two olefinic double bonds mention may be made of butadiene, isoprene, and 20 chloroprene.

The addition polymer may further include monomers having carboxylic, sulfonic or phosphonic acid groups. Carboxylic acid groups are preferred. Examples that may be mentioned include 25 acrylic acid, methacrylic acid, itaconic acid, maleic acid, and fumaric acid.

Examples of further monomers include hydroxyl-containing monomers, (meth)acrylamide or phenoxyethyl glycol 30 mono(meth)acrylate, glycidyl acrylate, glycidyl methacrylate, and amino (meth)acrylates such as 2-aminoethyl (meth)acrylate.

It is essential that in total from 0.1 to 30% by weight of the ethylenically unsaturated compounds of which the addition polymer 35 is composed are the monomers A defined at the outset.

The monomers A) do not include monomers having carboxylic acid or carboxylic anhydride groups.

40 Monomers A have a water solubility at 21°C of more than 5 g of monomer per liter (l) of water.

The water solubility is preferably more than 10 g/l of water.

45 Customary acrylic monomers on the other hand, such as C<sub>2</sub>-C<sub>18</sub> alkyl (meth)acrylates, have a water solubility well below 5 g/l.

Preferred monomers A are selected from the acrylic monomers. Particularly suitable are hydroxyalkyl (meth)acrylates, methyl (meth)acrylate, (meth)acrylonitrile, and (meth)acrylamide.

5 Particular preference is given to hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, methyl (meth)acrylate, (meth)acrylonitrile, and (meth)acrylamide.

Preferably from 0.5 to 20% by weight, with particular preference  
10 from 1 to 12% by weight, of the monomers are monomers A.

The addition polymer preferably has a K value of from 30 to 80, with particular preference from 40 to 60, measured in 1% solution (solvent: tetrahydrofuran, 21°C).

15 The K value according to Fikentscher is a measure of the molecular weight and the viscosity of the polymer.

The glass transition temperature ( $T_g$ ) of the addition polymer is  
20 preferably from -60 to +10°C, with particular preference from -55 to 0°C, with very particular preference from -55 to -20°C.

The glass transition temperature of the addition polymer can be determined by customary methods such as differential  
25 thermoanalysis or differential scanning calorimetry (see, e.g., ASTM 3418/82, midpoint temperature).

The UV-crosslinkable addition polymers can be prepared by copolymerizing the monomer components using the customary  
30 polymerization initiators and, if desired, using regulators, polymerization being carried out at the customary temperatures in bulk, in emulsion - for example, in water or liquid hydrocarbons - or in solution. The novel copolymers are preferably prepared by polymerizing the monomers in solvents, especially in solvents  
35 with a boiling range of from 50 to 150°C, preferably from 60 to 120°C, using the customary amounts of polymerization initiators, these amounts being generally from 0.01 to 10% by weight, in particular from 0.1 to 4% by weight, based on the overall weight of the monomers. Suitable solvents include in particular  
40 alcohols, such as methanol, ethanol, n- and isopropanol, n- and isobutanol, preferably isopropanol and/or isobutanol, and also hydrocarbons such as toluene and, in particular, petroleum spirits with a boiling range of from 60 to 120°C. It is also possible to use ketones, such as acetone and methyl ethyl ketone,  
45 and esters, such as ethyl acetate, and also mixtures of such solvents, preference being given to mixtures containing isopropanol and/or isobutanol in amounts of from 5 to 95% by

weight, in particular from 10 to 80% by weight, preferably from 25 to 60% by weight, based on the solvent mixture used.

In the case of solution polymerization, appropriate 5 polymerization initiators include, for example, azo compounds or ketone peroxides.

Following the polymerization in solution, the solvents can if desired be separated off under reduced pressure, operating at 10 elevated temperatures in the range, for example, of from 100 to 150°C. In this case the polymers can be used in the solvent-free state, i.e., as melts. In many cases it is also of advantage to prepare the novel UV-crosslinkable polymers by polymerization in bulk, i.e., without the use of a solvent, in which case it is 15 possible to operate batchwise or else continuously, in accordance, for example, with the information in US-A-4,042,768.

The addition polymer can be a melt, a solution in an organic solvent, or an aqueous dispersion and can be used in this form.

20 The polymers are preferably used in the form of a melt, i.e., in essentially solvent-free form (solvent content preferably less than 2% by weight based on the polymer).

25 The polymer can be applied to carriers, preferably from the melt, by usual techniques, such as brushing, rolling, flow coating, or knife coating, for example. In the case of the solution or aqueous dispersion, the solvent or water is removed, generally by drying.

30 In order to increase the flowability of the polymer, the temperature of the polymer in the case of application as a melt can be from 10 to 150°C, preferably from 50 to 150°C, with particular preference from 100 to 150°C.

35 Preferred film thicknesses are for example from 2 to 50 µm, with particular preference from 5 to 40 µm, with very particular preference from 10 to 30 µm.

40 Suitable carriers include, for example, labels made of paper or plastic, e.g., polyester, polyolefins or PVC, and also adhesive tapes or sheets of the above plastics.

45 Subsequently, the polymers are crosslinked with high-energy radiation, preferably UV light.

For this purpose, the coated carriers are generally placed on a conveyor belt and the conveyor belt is guided past a radiation source; for example, a UV lamp.

5 The degree of crosslinking of the polymers depends on the intensity and duration of irradiation.

The radiation energy is preferably in total from 100 to 1500 mJ/cm<sup>2</sup> of irradiated surface.

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The resulting, polymer-coated carriers can be bonded to moist substrates, especially refrigerated substrates. These substrates may, for example, be frozen product packaged with paper or with polymer films.

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Despite the moisture, and/or a film of water or layer of ice on the substrates, very good adhesion of the coated carriers, e.g., labels, is found.

20 The addition polymer is therefore suitable as an adhesive, or pressure-sensitive adhesive, especially hot-melt pressure-sensitive adhesive, for moist substrates, especially refrigerated substrates. In comparison to hot-melt pressure-sensitive adhesives based on

25 styrene-butadiene(isoprene)-styrene block copolymers, the addition polymers exhibit a much higher thermal stability and reduced strikethrough, by which is meant the penetration of the adhesive coating to the front face, the generally printed face of the carrier. In the case of paper labels in particular,

30 strikethrough results in an unwanted visual deterioration.

#### Examples

##### I) Addition polymers

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P1: Acrylic polymer composed of 91% by weight ethylhexyl acrylate and 9% by weight hydroxyethyl acrylate

C1: Acrylic polymer composed of 100% by weight ethylhexyl

40 acrylate

The polymers were prepared by conventional solution polymerization with subsequent distillative removal of the solvent.

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## II) Preparation of the coated carriers and testing

The polymers P1 and C1 were each coated from the melt onto label paper at a temperature of 120°C. The film thickness was 20 µm.

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The coated label paper was irradiated with UV light and the polymer was crosslinked.

The label paper was bonded to a polyethylene plate and the force required for peeling, in N/25 mm, was determined using a tensile testing machine.

The experiment was carried out at different temperatures of the polyethylene surface:

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	+25°C	+5°C	-20°C	-10°C *
P1	4.2	5.8	3.7	3.6
C1	1.9	3.5	3.3	3.0

20 \* The polyethylene surface was first wetted so that a coherent film of water formed.

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